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X-ray diffraction studies of azo schiff base

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Abstract : An X-ray diffraction study has been carried out for 4-[2' hydroxy salicylidene 5'-(2''-thiazolylazo)] toluene. This ligand was synthesized by condensing 5'-(2'-thiazolylazo) salicyladehyde and *p* toluidine. The purified sample has been subjected for structural characterization. The structure of compound is found to be tetragonal belonging to non-primitive system. The strain broadening effects are also examined and discussed.

Keywords : Azo schiff base, X-ray diffraction, strain broadening

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Schiff bases and thiazole compounds bearing azo and azomethine groups are known to possess bacteriostatic, anticancerous and other bio-chemical properties [1-4]. To know the details about coordinating behavior of ligands containing this important functional group, one of such ligands 4-[2' hydroxy salicylidene 5'-(2''-thiazolylazo)] toluene has been undertaken by us in this laboratory for the detailed study of structural properties. In this present investigation, we report the X-ray diffraction studies of this ligand.

All the chemicals used were of AR grade. 5-(2'-thiazolylazo) salicylaldehyde was prepared as per the procedure reported [5]. The schiff base ligand was synthesized by dissolving 5-(2'-thiazolylazo) salicylaldehyde (5 g, 0.02 mole) in ethanol (100 cm^3), to this, a solution of *p*-toluidine (2.298 g 0.02' mole) in ethanol (10 cm^3); was added and resulting mixture was refluxed for 3 h. on water bath. After cooling, the solution was poured in ice-cold water, the separated solid was filtered, dried and purified by repetitive recrystallisation from ethanol. The purity was checked by thin layer chromatography (TLC).

Colour, yield, melting point and elemental analysis are as follows :

Dark red, yield 72%, Mp. – 142°C, IR – 1619 cm^{-1} (ν C=N), 1590 cm^{-1} (ν N=N), 1280 cm^{-1} (νC-O). Anal. Cald. for $C_{17}H_{14}N_4OS$, C : 63.31% H : 4.37%, N : 17.38% found C : 63.80%, H : 4.29%, N : 17.49%.

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Structure of the ligand was tentatively fixed as given in Figure 1 on the basis of elemental analysis of IR, UV and ^{1}HNMR spectral studies.

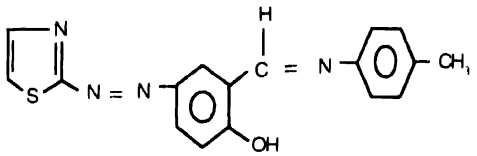

Figure 1. Structure of ligand

The XRD spectra of ligand was recorded in the range from 10^0 to 80^0 (2θ) on Philips PW 3710 diffractometer attached to digitized computer along with graphical assembly in which CuKα radiation source connected with the tube Cu-Ni 25 kV/20 mA was used.

The X-ray diffractogramme of 4 [2' hydroxy salicylidene 5'-(2'' –thiazolylazo)] toluene shown in Figure 2. The XRD pattern shows twelve reflection peaks between the range of 10^0 and 80^0 (2θ) with maxima at $2\theta = 14.365^0$ corresponding to a value of d = 6.1606 Å.

The 2θ values for prominent peaks are listed in Table 1. All main peaks have been indexed by using computer software and

trial and error method keeping in mind the characteristic of various symmetry system till a good fit could be obtained between observed and calculated d and Q values. The method

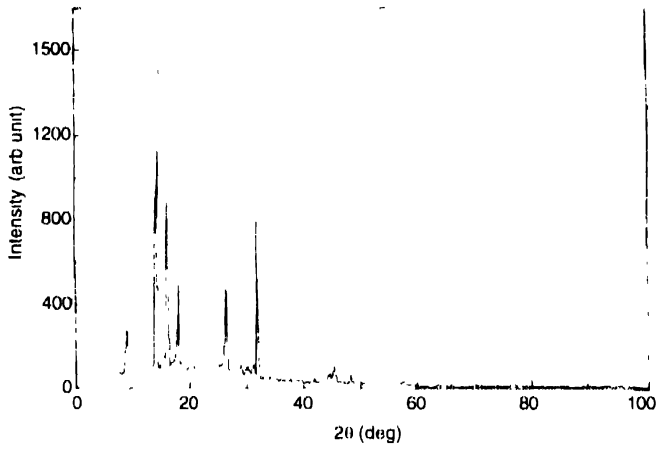

Figure 2. X-ray diffractogramme of ligand

also yielded *hkl* (miller indices) values. The relative intensities corresponding to the prominent peaks have been also calculated. (Table 1).

Table 1 Powder X-ray diffraction data of 4-[2'-hydroxy salicylidene 5'-(2''-thiazolylazo)] toluene

Peak No	2θ deg	d_{obs}	d_{cal}	Q_{obs}	Q_{cal}	*hkl*	*RI*
1	8 98	9 8336	9 8336	0 0103	0 0103	001	13 7
2	9 14	9 6725	9 6725	0 0106	0 0106	110	25 0
3	14 36	6 1606	6 1174	0 0263	0 0267	210	100 0
4	15 85	5 5865	5 6149	0 0320	0 0317	201	10 3
5	16 35	5 4168	5 1943	0 0340	0 0370	211	63 8
6	18 06	4 9076	4 9168	0 0415	0 0413	002	52 4
7	25 98	3 4278	3 4197	0 0851	0 0855	400	9 4
8	31 17	2 8669	2 8892	0 1216	0 1197	213	5 7
9	31 90	2 8034	2 8075	0 1272	0 1268	402	41 5
10	43 99	2 0564	2 0631	0 2364	0 2349	324	5 6
11	45 47	1 9928	1 9961	0 2518	0 2509	404	9 8
12	48 38	1 8799	1 8790	0 2829	0 2832	720	6 4

The observed and calculated values of d and Q of the present sample indicate that there is close agreement between observed and calculated values of d and Q by assumption of tetragonal system to give a unit cell [5] with lattice constants $a = b =$ 13.6709 Å, $c = 9.8336$ Å and cell volume $V = 1839.90$ Å^3. The unit cell parameters were refined by weight fraction method. Such refined parameters were used for finding out space group and Laue group from international table of X-ray crystallography[6]. In conjugation with such cell parameters, the condition [7,8], such as $a = b \neq c$ and $\alpha = \beta = \gamma = 90^0$ required for the sample to be tetragonal, were tested and found to be in good agreement.

The experimental value of density (ρ) has been calculated by using specific gravity method. The number of atoms per unit cell n was calculated by using the equation ($n = \rho$ NV / M) where ρ is density, M is the molecular weight, V the unit cell volume and N the Avogadro number. With this n value, the theoretical density was calculated. The calculated density values are in good agreement with the experimental values. The other parameters such as pore fraction, packing fraction, particle size, and radius of atom were then calculated. All these values are presented in Table 2.

Table 2. X-ray parameters of 4-[2' hydroxy salicylidene 5'- (2''-thiazolylazo)] toluene

Structure	Tetragonal
Space group	I4/ mmm
Laue group	4/m
Point group	4/mmm
Symmetry of lattice	Non primitive
Lattice parameters	13 679 Å
	9 933 Å
Bond angles	$\alpha = \beta = \gamma = 90^0$
Vol of unit cell	1839 90 Å^3
Radius of atom	5 9231 A
Vol of atom	870 40 Å^3
Packing fraction	47 30 %
Density ρ (experimental	0 532 gr/cc
(theoretical)	0 581 gr/cc
Pore fraction	33 73 %
Thickness of particle	249 05 Å

The particle size of the sample was calculated by using an equation $t = 0.9\ \lambda\ /$ B cos θ. The parameters can distinguish

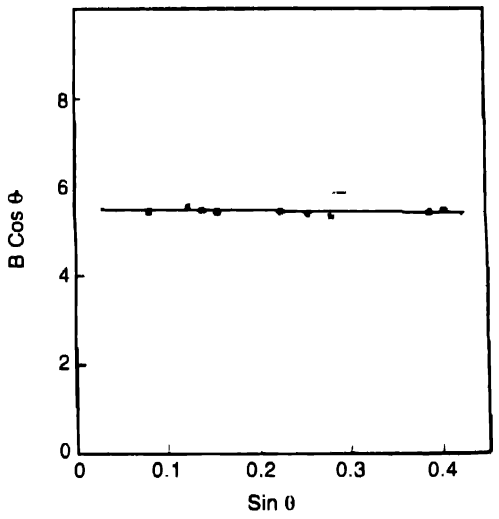

Figure 3. Analysis of homogeneity.

between natural particle size and particle size due to broadening effect. This was done by calculating full width at half maximum (B) corresponding to its Bragg's θ values. The nature and behavior of these values for the present ligand are shown graphically in Figure 3.

A plot of B $\cos\theta$ *versus* $\sin\theta$ was found to be a straight line parallel to X-axis indicating an absence of any strains caused by inhomogeneous lattice distortions and compositional fluctuations. Hence, present sample seems to be homogeneous with respect to the particle size distribution.

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References

[1] R D Ghilard and C T Stears R Price in *Comprehensive Coordination Chemistry* (ed) Wilkinson (Oxford Pergamon) **Vol.6** (1987)

[2] M A Pujar, B S Hadimani, S Meena Kumar, S M Gaddad and Y F Neelgund *Curr Sci.* **55** 353 (1986)

[3] P P Hankare, R K Patil, S S Chavan, A H Jagtap, and B S Battase, *Indian J Chem* **104** 1326 (2001)

[4] P C Joshi *J Indian Chem Soc* **55** 467 (1978)

[5] S S Chavan P P Hankare, A H Jagtap and R T Pattar *Indian J Phys* **75A** 273 (2001)

[6] J D H Donney and David Haker *Tables of Space and Group Criteria Crystallographiques Naturalist Canadian* **67** p33 and pl60 (1940)

[7] B D Cullity *Element of X ray Diffraction* (London Wesley) (1959)

[8] S Perser, H P Rooksby and A J C Wilson *X-ray Diffraction by Polycrystalline Materials (Institute of Physics* London) p344 (1955)